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BURNING RATE STUDIES OF HMX PROPELLANTS AT HIGH PRESSURES

INTERIOR/EXTERIOR BALLISTICS BRANCH
GUNS, ROCKETS AND EXPLOSIVES DIVISION

MARCH 1975

FINAL REPORT: OCTOBER 1973 - NOVEMBER 1974

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Burning rate studies of some nitramine propellants were conducted at pressures from 2,000 to 50,000 psi. Changes in HMX particle size distribution produced large effects on the burning rates and burning rate exponent at pressures below 7,000 psi, but had negligible effects at pressures above 7,000 psi. None of the ballistic modifiers evaluated were effective in eliminating the slope break or in reducing the burning rate slope below 1.0.

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PREFACE

This report documents work performed at the Air Force Armament Laboratory, Armament Development and Test Center, Eglin Air Force Base, Florida, between October 1973 and November 1974 in support of Project 25470702. Mr. Bertram K. Moy (DLDL) was program manager for this effort.

This technical report has been reviewed and is approved for publication.

FOR THE COMMANDER

A. D. Brown Jr

ALFRED D. BROWN, JR., Colonel, USAF
Chief, Guns, Rockets & Explosives Division

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SECTION I

INTRODUCTION

The objective of current advanced gun propellant development is to increase propellant impetus while decreasing propellant flame temperatures. These efforts have largely been dictated by the increasing emphasis on rapid fire weapons and projected requirements for higher muzzle velocities. In order to achieve this objective, propellant contractors have been evaluating linear and cyclic nitramines in nitrocellulose and hydrocarbon formulations. However, ballistic tests have indicated that these nitramine propellants exhibit a ballistic phenomenon which is detrimental to its performance in guns. This phenomenon is the rapid change in pressure dependence of burning rate in the 3,500 to 5,000 psi pressure region, resulting in high chamber pressures and poor ballistic efficiencies.

The combustion processes of nitramine propellants have only recently begun to be extensively studied and, as a result, they are not well understood. There has been only limited ballistic study done at pressures above 8,000 psi. This report discusses the burning rate studies of propellants made and tested at the Air Force Armament Laboratory (AFATL), Armament Development and Test Center, Eglin Air Force Base, Florida. The tests were conducted throughout the entire pressure range seen in the gun environment. The dependence of burning rate and burning rate exponent on HMX particle size was examined. Three additives known to change the burning rate exponent of ammonium perchlorate and ammonium nitrate propellants were evaluated. Low melting organic compounds were added to the formulations to test the hypothesis that these compounds would wet and encapsulate the HMX crystals and promote normal propellant burning at high pressures.

SECTION II

TECHNICAL DISCUSSION

It has been shown (References 1, 2, 3) that advanced gun propellants containing linear and cyclic nitramines have burning rate pressure exponents which change in the 5,000 psi pressure region and which are greater than one. These pressure exponents are unacceptable for gun applications because they cause high chamber pressures and poor ballistic efficiencies. It is then important to determine accurately the pressures at which the pressure exponent changes and what the exponent is throughout the complete pressure cycle of a gun firing.

Studies were initiated at AFATL to determine some of the ballistic characteristics of nitramine propellants and to evaluate various additives which would alter the characteristics. These studies would then lead to a better understanding of the combustion mechanism of the nitramines. Burning rate data for gun propellants have traditionally been derived from closed bomb firings. The data were calculated from an analysis of the slope of the pressure-time trace produced on the oscilloscope. This analysis was predicated on the assumption that all the propellant grains ignited simultaneously and that the propellant burned uniformly. Due to the interpretative nature of the closed bomb burning rate determination process, it was decided that strand burning rates were required to generate true propellant burning rates at specific pressures. To this end, AFATL designed and purchased a propellant strand burner (Appendix A) which would provide linear burning rate data from 2,000 psi to 50,000 psi. This device would have steady state capability of simulating propellant behavior at gun pressures. Using this equipment, AFATL was able to conduct combustion studies of experimental gun propellants in support of contract and in-house programs.

The binder used for all in-house propellant work was R-45M (a hydroxy-terminated polybutadiene) and TDI (tolylene diisocyanate). Burning rate studies were conducted to determine the differences in burning rate between RDX and HMX propellants. Batches were made with a bimodal distribution of

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References:

1. The title of this reference is available to qualified agencies upon request to AFATL (DLDL), Eglin Air Force Base, Florida 32542.

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3. The title of this reference is available to qualified agencies upon request to AFATL (DLDL), Eglin Air Force Base, Florida 32542.

Class A/E[1] (70/30) RDX and HMX at an 80 percent solids loading. The RDX propellant had higher burning rates (Figure 1, Table 1) throughout the entire pressure range. The slope break region for the RDX propellant probably occurred below 2,000 psi. The pressure exponents of both of these RDX and HMX propellants were near or greater than 1.0 and were unacceptable for gun propellants.

The effects of HMX particle size on the burning rate slopes and the onset of slope break were determined at an 80 percent solids loading. This solids loading was near stoichiometry and could be readily processed for burning rate strands. The variation in particle size was effected by changing the ratio of Class A[1] to Class E[1] HMX. One batch containing 5-micron unimodal HMX was prepared by researchers at Lockheed Propulsion Company, Redlands, California, and evaluated at pressures of 3,000 psi and above. The burning rates of propellants made with larger particle size HMX are higher than those of propellants made with smaller particle sizes (Figure 2, Table 2). The onset of slope break appears to be shifted to higher pressures with decreasing particle size. The data in Table 2 indicated that lower burning rate slopes were achieved with smaller HMX particles at pressures below 5,000 psi. Above 5,000 psi, no significant changes in slope were evident in changing from Class A[1] HMX down to 5-micron HMX. At pressures above 10,000 psi the decomposition mechanism appears to be that of HMX itself, yielding a slope of approximately 1.0.

A variety of compounds have been used in the rocket propellant industry to alter the burning rate slopes of propellants containing ammonium perchlorate and ammonium nitrate oxidizers. Some of these compounds were evaluated with HMX to determine their effect on the mode of decomposition of HMX propellants. Three of these compounds, titanium dioxide, ammonium persulfate and ammonium sulfate, were evaluated at the 2 percent level in propellants containing 80 percent HMX. Titanium dioxide shifts the onset of the slope break of ammonium perchlorate propellants from 4,500 to 8,000 psi. Ammonium persulfate increases the burning rate slope of ammonium nitrate propellants. Ammonium sulfate reduces the slope of ammonium perchlorate propellants to less than 0.10 in the 1,000 psi region. The burning rate data in Table 3 indicates that these compounds had little or no effect on the burning rate and the burning rate slopes of HMX propellants. The mechanism of decomposition of HMX was apparently different from that of either ammonium perchlorate or ammonium nitrate.

It was reported (Reference 4) that formaldehyde accelerated the decomposition of RDX. Since HMX was analogous to RDX, it was possible that the combustion characteristics of HMX propellant could be altered through

Footnote:

[1]Class A - Average Particle Size - 150 microns
Class E - Average Particle Size - 14 microns

References:

4. Cosgrove, J.D., and Owen, A.J., The Thermal Decomposition of 1,3,5 Trinitrohexahydro 1, 3, 5 Triazine, Part I and Part II, Combustion and Flame 22, 13-22 ERDE, 1974.

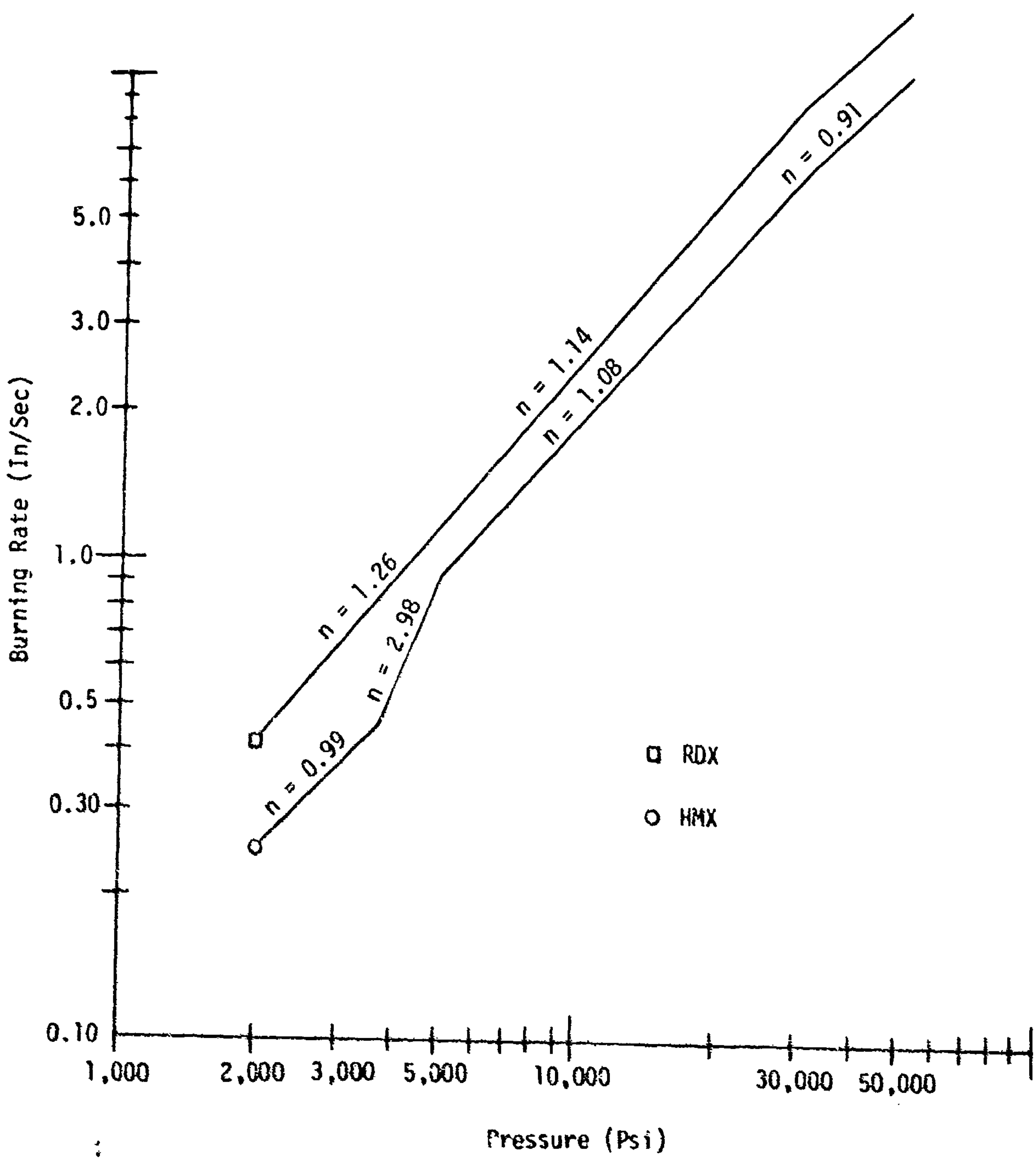
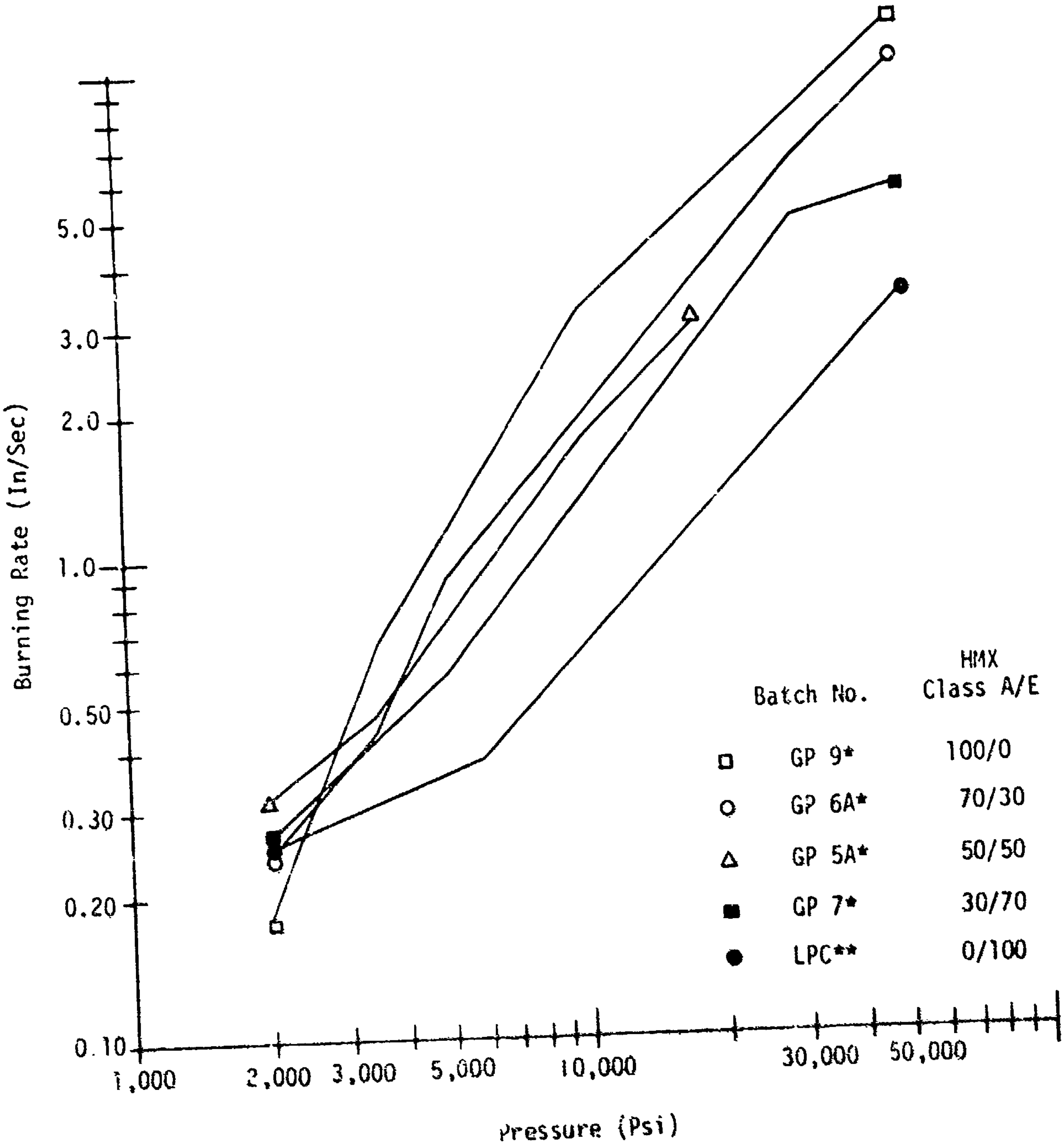


Figure 1. Burning Rates of Nitramine Propellants [80 Percent Solids (Class A/E, 70/30), 20 Percent R-45M/TDI]



Pressure Range, (Kpsi)	Slope GP9	6A	5A	7	LPC
2.0 - 3.5	2.46	0.99	0.82	0.78	0.45
3.4 - 5.0	1.58	2.48	1.25	0.78	0.37
7.0 - 10.0	1.58	1.08	1.25	1.20	1.00
10.0 - 20.0	0.86	1.08	0.92	1.20	1.00

* 80 Percent HMX

** Lockheed Propellant, 75 Percent 5-Micron HMX

Figure 2. Effect of Particle Size on Burning Rates of HMX/R-45M Propellants

TABLE 1. BURNING RATES OF NITRAMINE PROPELLANTS

[80 Percent Solids (Class A/E, 70/30), 20 Percent R-45M/TDI Binder]

Nitramine	RDX	HMX
Pressure (Psi)	Burning Rate @ 70°F (In/Sec)	
2,000	0.41	0.24
5,000	0.82	0.88
10,000	2.60	1.91
30,000	8.70	6.24
50,000	13.97	10.00
Pressure Range (Psi)	Burning Rate Slope	
2,000 - 3,500	1.26	0.99
3,500 - 5,000	1.14	2.48
5,000 - 30,000	1.14	1.08
30,000 - 50,000	0.88	0.91

TABLE 2. EFFECT OF PARTICLE SIZE ON THE BURNING RATES OF HMX PROPELLANT[1]

HMX					
Class A	100	70	50	30	--
Class E	0	30	50	70	--
5 Micron	--	--	--	--	100[2]
Pressure (Psi)	**Burning Rate @ 70°F (In/Sec)**				
2,000	0.18	0.24	0.31	0.26	0.25
5,000	1.10	0.88	0.74	0.57	0.36
10,000	3.13	1.91	1.73	1.32	0.64
30,000	8.00	6.24	--	4.80	1.95
50,000	12.80	10.00	--	5.50	3.32
Pressure Range (Psi)	**Burning Rate Slope**				
2,000 - 3,500	2.46	0.99	0.82	0.78	0.45
3,500 - 5,000	1.58	2.48	1.25	0.78	0.37
5,000 - 7,000	1.58	1.08	1.25	1.20	--
7,000 - 10,000	1.58	1.08	1.25	1.20	1.00
10,000 - 20,000	0.86	1.08	0.92	1.20	1.00
20,000 - 30,000	0.86	1.08	--	1.20	1.28
30,000 - 50,000	0.86	0.91	--	0.23	1.28

[1] 80 percent HMX

[2] 75 percent HMX (Unimodal 5-Micron)

TABLE 3. EFFECT OF BALLISTIC MODIFIERS ON THE BURNING RATES OF HMX PROPELLANTS

[80 Percent HMX (Class A/E, 70/30), 2 Percent Additive]

Additive	None	TiO_2	$(NH_4)_2S_2O_8$	$(NH_4)_2SO_4$	Celcon®
Pressure (Psi)	Burning Rate @ 70°F (In/Sec)				
2,000	0.24	0.30	0.22	0.24	0.26
5,000	0.88	0.88	0.81	0.70	0.87
10,000	1.91	1.98	2.07	1.93	2.21
30,000	6.24	6.90	6.46	6.40	6.76
50,000	10.00	10.05	11.76	10.90	10.40
Pressure Range (Psi)	Burning Rate Slope				
2,000 - 3,500	0.99	1.00	1.28	1.01	1.14
3,500 - 5,000	2.48	1.49	1.57	1.98	1.62
5,000 - 7,000	1.08	1.12	1.57	1.30	1.62
7,000 - 10,000	1.08	1.12	1.01	1.30	1.00
10,000 - 20,000	1.08	1.12	1.01	1.30	1.00
20,000 - 30,000	1.08	0.79	1.01	1.30	1.00
30,000 - 50,000	0.91	0.79	1.01	0.82	0.86

the introduction of formaldehyde into the burning process. Celcon,® a polyacetal (manufactured by Celanese Corporation) which decomposes to formaldehyde, was incorporated into an HMX/R-45M propellant. The burning rate data (Table 3) indicates that, although the burning rate slope was lower (1.62 versus 2.48) in the 3,500 to 5,000 psi range, no significant changes were seen in the slope at pressures greater than 7,000 psi. Throughout the entire pressure range of 2,000 to 50,000 psi the burning rates of the propellant with Celcon® were essentially the same as those of the control propellant. The data indicates that the catalytic effect of formaldehyde on the decomposition of HMX must be slower than the decomposition mechanism of HMX.

One of the explanations advanced for the slope break phenomenon of HMX propellants (Reference 5) was that at high pressures the HMX crystals were burning independent of the propellant binder. "At low pressures, the strand is able to burn as a propellant because the binder is able to melt and fill the crystal interstices, wetting and encapsulating the crystals to a certain depth beneath the surface, forming a composite that did not fully exist in the original cured propellant. At some high pressure, the burning rate of the HMX is fast enough to lead the development of the binder melt such that the strand is able to burn as an HMX strand depending upon the extent of crystal contact and void interstices in the original propellant". It was decided to test this postulate by evaluating the effect of low melting crystalline compounds on the burning rate slope of an HMX/R-45M propellant. At low temperatures these compounds could melt and encapsulate the HMX crystals, separating them from each other. Because this separation of HMX crystals from each other was independent of binder melt, propellant burning should take place rather than HMX burning. The compounds selected for evaluation were:

	Melting Point (°C)	Boiling Point (°C)
acetanilide	113	307
anthracene	216	340
phenylsulfone	125	377
hydroquinone	170	285

Prior to mixing propellants containing these compounds, stability studies using differential scanning calorimetry tests were conducted on propellant from small hand mixed batches. The heating rate was 10°C/min on 2-mg size samples. Acetanilide and phenylsulfone, the two very low melting compounds, greatly suppressed the HMX exotherm peak (Figure 3). However, this change in the HMX peak did not appear to affect the propellant burning rates. Propellants containing 2 percent of the compounds were mixed and prepared for testing at 70°F between 2,000 and 50,000 psi. The data in Table 4

References:

5. Cohen, Norm, Combustion of Nitramine Propellants, LPC 744-OPR-2, 30 August 1974.

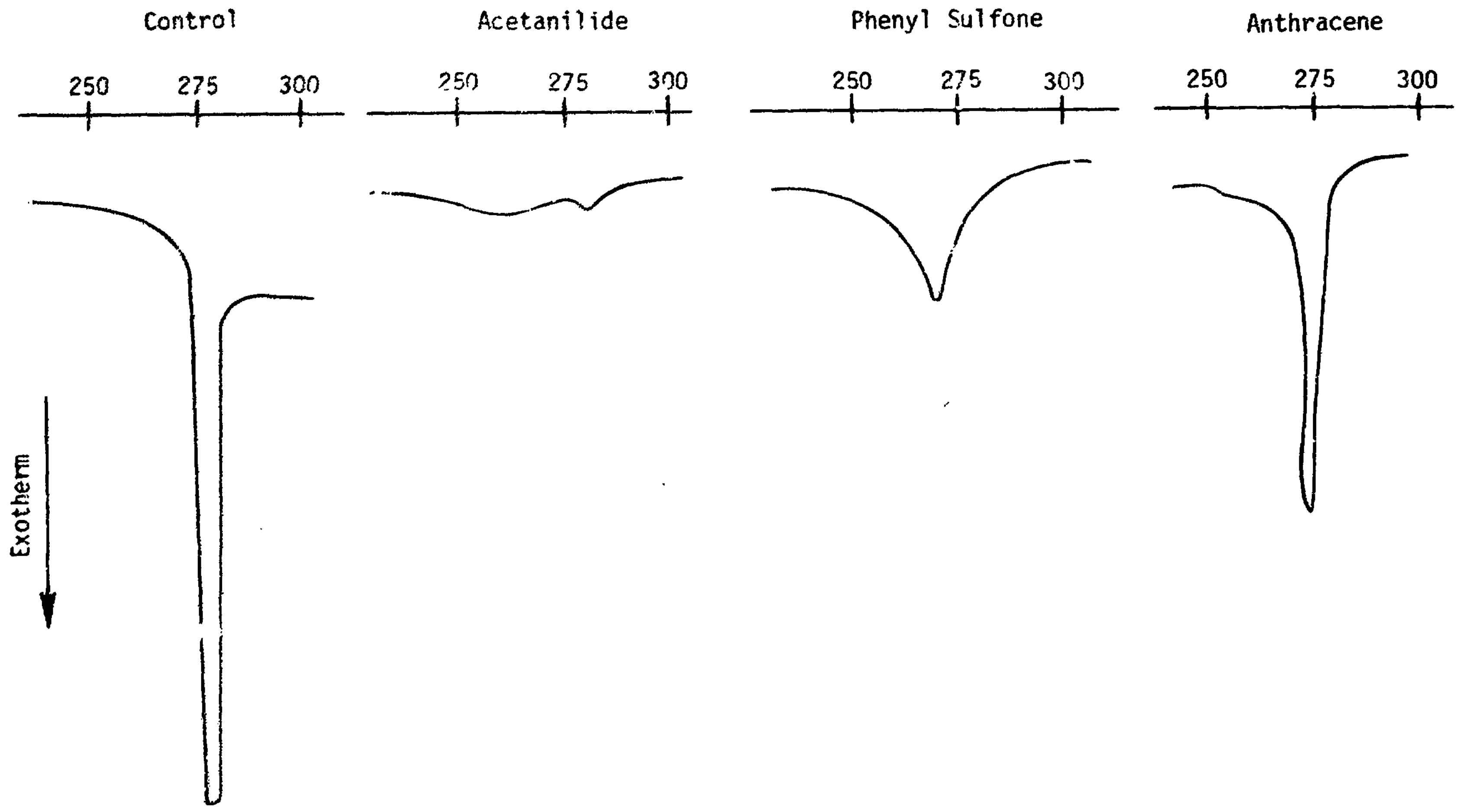


Figure 3. Effect of Additives on the Differential Scanning Calorimeter Curve of an HMX Propellant
(80 Percent HMX, 2 Percent Additive, 18 Percent R-45M/TDI Binder)

TABLE 4. EFFECT OF ADDITIVES ON THE BURNING RATES OF HMX PROPELLANT

[80 Percent HMX (Class A/E, 70/30), 2 Percent Additive]

Additive	None	Acetanilide	Anthracene	Phenyl Sulfone	Hydro-Quinone
Pressure (Psi)			Burning Rate @ 70°F (In/Sec)		
2,000	0.24	0.30	0.22	0.25	0.21
5,000	0.88	0.95	0.88	0.87	0.70
10,000	1.91	2.10	2.15	1.84	1.97
30,000	6.24	6.20	6.76	5.60	6.64
50,000	10.00	10.35	11.36	9.60	10.73
Pressure Range (Psi)			Burning Rate Slope		
2,000 - 3,500	0.99	1.25	1.02	0.89	1.00
3,500 - 5,000	2.48	1.25	2.10	2.06	1.83
5,000 - 7,000	1.08	1.14	1.36	1.10	1.83
7,000 - 10,000	1.08	1.14	1.36	1.00	1.06
10,000 - 30,000	1.08	0.99	1.07	1.00	1.06
30,000 - 50,000	0.91	0.99	1.07	1.00	0.90

indicates that, although there were some changes in the burning rate slope between 3,500 and 5,000 psi, the burning rates and burning rate slopes of the propellant were not significantly affected by the addition of the low melting compounds. All the burning rate slopes above 10,000 psi were still approximately 1.0. This does not necessarily disprove the postulate since (1) the concentration of the additives may have been too low to be effective, or (2) the heat transfer required to melt the compounds may not have been as fast as the decomposition of HMX.

Laboratory studies to characterize the combustion processes of HMX propellants are continuing. It would be desirable to find a compound or class of compounds that would reduce the burning rate slope of HMX propellants. It is necessary to find compounds which will affect the slope, one way or another. Before an understanding of the mechanism can be achieved, some compound or family of compounds must be found which will alter the combustion mechanism. Once these compounds have been identified, a correlation can be established between their properties, molecular make-up and effectiveness in alteration of the combustion process. These data may provide the key to understanding the combustion mechanism of HMX.

SECTION III

SUMMARY

Burning rate studies of nitramine propellants were conducted at pressures from 2,000 to 50,000 psi. When the tests were conducted at pressures in the slope break region, abnormal data scatter was observed. Slight changes in pressure in these regions produced large changes in burning rates. Changes in HMX particle size distribution had significant effects on the burning rates and burning rate slopes at pressures below 7,000 psi. At pressures above 7,000 psi, the HMX particle size distribution had little effect on the burning rate slopes of the experimental propellants. Ammonium sulfate, ammonium persulfate, titanium dioxide, Celcon®, acetanilide, phenylsulfone, anthracene and hydroquinone were evaluated as additives in the propellant. None of these were effective in eliminating the slope break or in reducing the burning rate slope to less than 1.0.

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APPENDIX A

PROPELLANT STRAND BURNER

The high pressure propellant strand burner was designed by AFATL personnel and built by Autoclave Engineers, Erie, Pennsylvania. It can be used to test strands up to 1/4 inch in diameter and up to 6 inches in length and at any pressure up to 50,000 psi. The unit consists of four subassemblies: (1) control panel (Figure A-1), (2) intensifier (Figure A-2), (3) storage assembly (Figure A-2), and (4) test assembly (Figure A-3).

1. Control Panel

The control panel houses the electrical hardware which actuates the valves to direct the flow of nitrogen between the storage tanks and the strand burner. There are six digital readouts to indicate pressures in the storage and surge tanks, strand burner, and in the lines. A frequency counter is used to determine the burning time. A comparator is incorporated into the system which shuts the intensifier off when the designated pressure in the storage tank has been achieved. Transfer of nitrogen pressure in and out of the strand burner is done remotely.

2. Intensifier

The intensifier is a two-stage gas booster for service with inert gases to a maximum of 60,000 psi. It uses nitrogen at inlet pressures between 1,000 and 2,500 psi. Inlet pressures lower than 1,000 psi cause rapid deterioration of the seals. One side of the two-stage gas compressor raises the pressure to a maximum of 10,000 psi, while the other side raises it to a maximum of 60,000 psi. The gas can be pumped into the storage tank, storage and surge tanks, storage and strand burner, or just the strand burner.

3. Storage Assembly

The storage assembly consists of two 600-cubic-inch stainless steel cylinders and six high pressure valves. One of the cylinders is used for the storage tank and the other is used for the surge tank. The storage tank can be pressurized while the strand burner is being cleaned. Gases can then be bled into the burner. Additional gases from the combustion process are bled into the surge vessel. At pressures below 10,000 psi the pressure surge is about 150 psi. The maximum pressure rise at 50,000 psi is about 350 psi. The cylinders were hydrotested to 100,000 psi, while the stainless steel lines are rated at 62,000 psi. There are six 50,000 psi diaphragm valves. Five are normally closed and require 75 psi air pressure to open, while one is open and requires air pressure to close. When air pressure is lost, the entire system is vented.

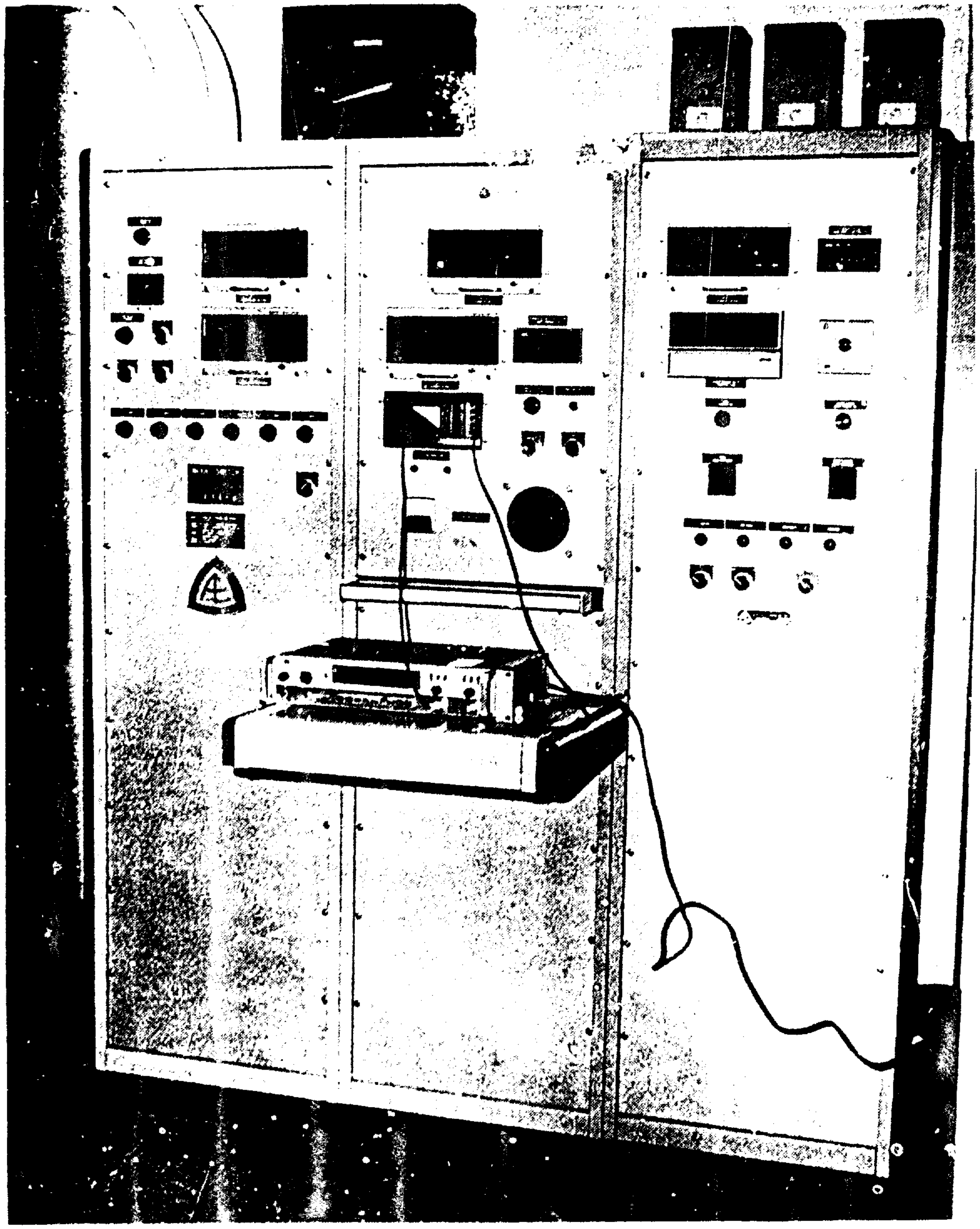

Figure A-1. Propellant Strand Burner Control Panel

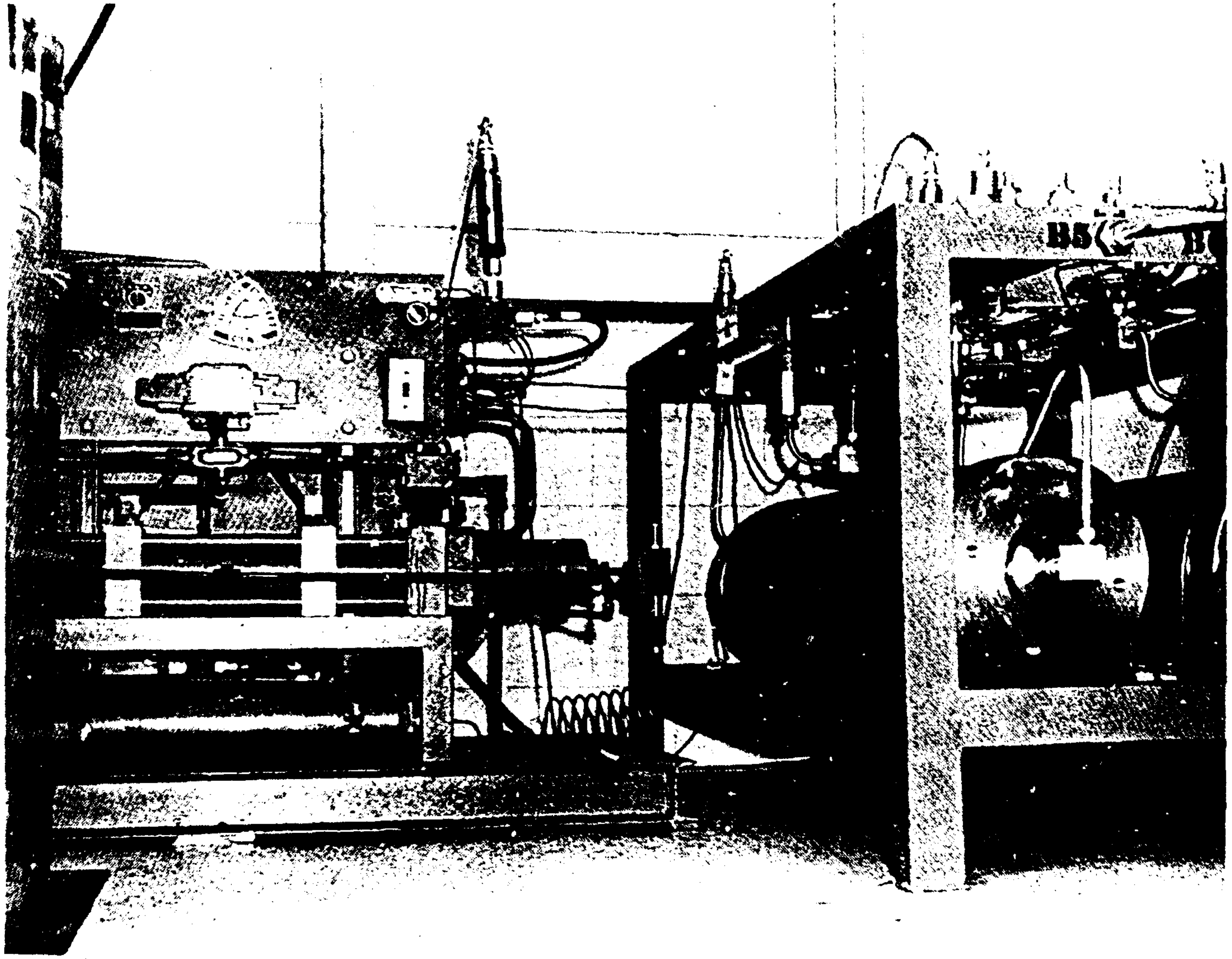

Figure A-2. Propellant Stra ' Burner Intensifier and Storage Assembly

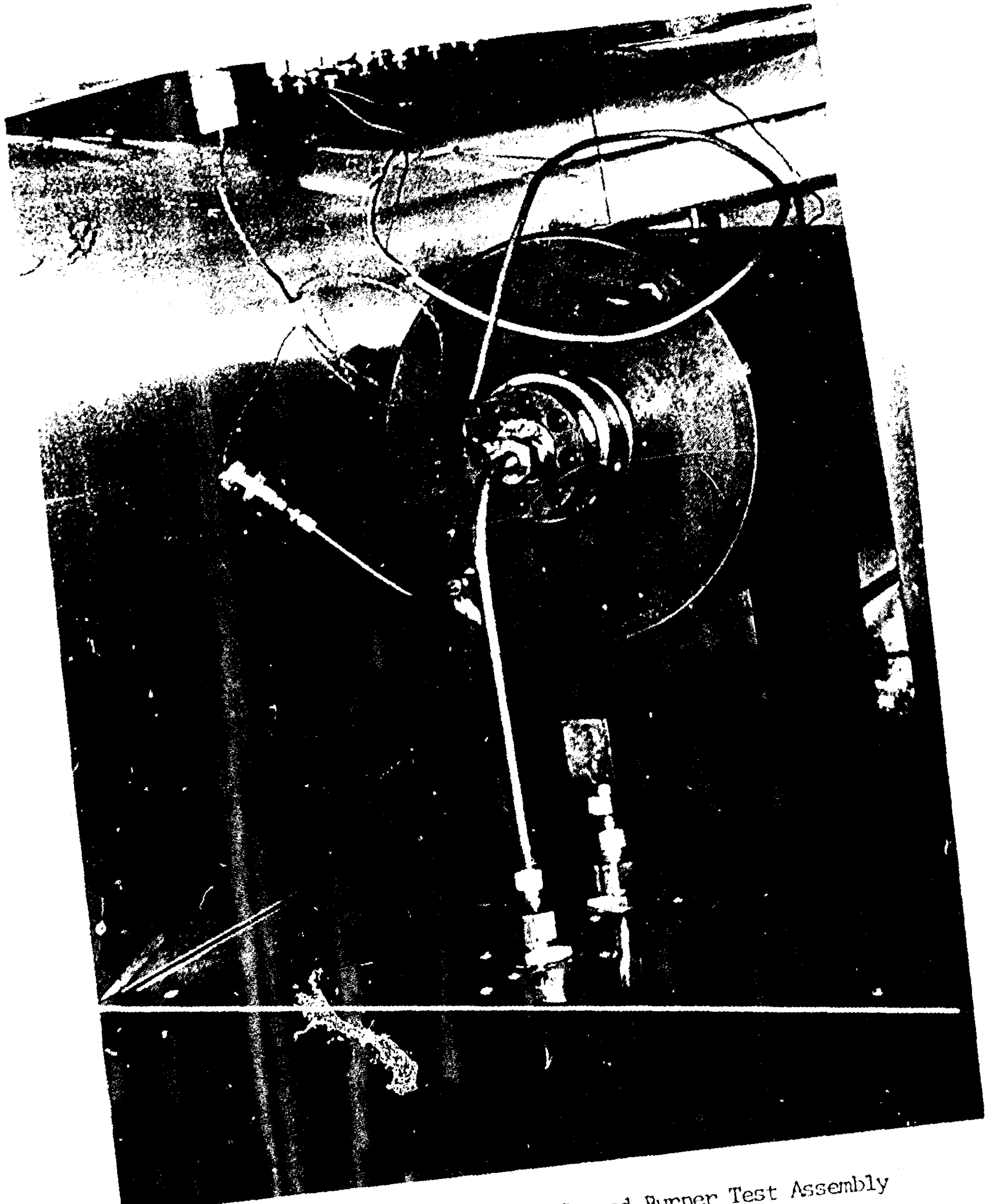

Figure A-3. Propellant Strand Burner Test Assembly

4. Test Assembly

The test assembly consists of a bomb head installed in an 88-cubic-inch chamber. It is housed in a conditioning cabinet which can vary the temperature between -65°F and +200°F. Although the strand holder is fairly standard, the rest of the bomb head differs from conventional bomb design. The metal seal for the bomb head is a soft metal ring which is forced up against the head to effect the seal. The wires are brought through the head and soldered to tapered plugs which are pushed into place by the internal pressures of the gas which are bled into the test assembly. Most of the electrical and sealing problems encountered to date have been caused by these plugs. The data generated from the test assembly has been fairly reproducible throughout the pressure range of 2,000 to 50,000 psi. Exceptions to this occur when the tests are run in the slope break regions. Data scatter is accentuated when the slope break is steep.

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REFERENCES

1. The title of this reference is available to qualified agencies upon request to AFATL (DLDL), Eglin Air Force Base, Florida 32542.

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5. Cohen, Norm, Combustion of Nitramine Propellants, LPC 744-OPR-2, 30 August 1974.

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Hq PACAF/LGWLE	4
USAFTAWC/AY	1
TAWC/TRADOCLO	1
AFATL/DL	1
AFATL/DLB	1
AFATL/DLOU	1
AFATL/DLOSL	2
AFATL/DLDL	20
AFATL/DLDE	1
ADTC/WE	1
AFATL/DLDG	1
AFIS/INTA	1

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